

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicants: Shau-Lin Franklin Chen et al. Examiner: Cam N. Nguyen  
Serial No.: 10/812,542 Group Art Unit: 1754  
Filed: March 30, 2004 Docket: 4932/ENG0104-00US  
Conf. No.: 3423  
Title: Exhaust Gas Treatment Catalyst

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DECLARATION UNDER 37 C.F.R. §1.132

Commissioner for Patents  
P.O. Box 1450  
Alexandria, VA 22313-1450

Sir:

I, Robert Farrauto, hereby declare that:

1. I am a citizen of the United States residing in Princeton, New Jersey.
2. I received my undergraduate degree in Chemistry from Manhattan College in 1964, and my Ph.D. from Rensselaer Polytechnic Institute in 1968.
3. Presently, I am employed as a Research Fellow at the Corporate Research Laboratories of BASF Catalysts (formerly Engelhard Corporation) in Iselin, New Jersey, USA, the assignee of the present patent application. My major responsibilities have included the development of advanced automobile emission control catalysts and catalysts for the chemical industry. I managed an Engelhard research team that developed and commercialized diesel oxidation catalysts for the European, North American and Asian markets for passenger cars and heavy duty trucks.
4. I currently manage a research team of 15 scientist and engineers developing new catalyst technology for the hydrogen economy including hydrogen refueling stations and fuel cells for stationary, portable power and vehicular applications.
5. I am an Adjunct Professor in the Earth and Environmental Engineering Department of Columbia University, in the City of New York where I teach courses in catalysis
6. I am a co-author of two books pertaining to catalyst technologies, including Catalytic Air Pollution Control, New York: Wiley-Interscience, 2002 ("the book"). I am also the author or co-author of over 75 publications, and I am an inventor or co-inventor of about 50 United States Patents.

7. I have reviewed the pending claims in the patent application, the Final Office, mailed on November 2, 2007, and the cited reference, U.S. Patent No. 5,556,825 to Shelef et al., ("Shelef"), relied upon in rejecting the pending claims in the above-referenced application. The Shelef reference does not teach or suggest the claimed invention of the instant patent application.

8. The only independent claim in the patent application, claim 1, recites:

An exhaust gas treatment catalyst comprising: (a) a carrier; (b) a first washcoat layer deposited on the carrier, said first washcoat layer comprising substantially only at least one refractory metal oxide; (c) a second washcoat layer deposited on the first washcoat layer, said second washcoat layer comprising substantially only at least one oxygen storage component and at least one binder therefor; and (d) a third washcoat layer deposited on the second washcoat layer, said third washcoat layer comprising at least one layer of one or more platinum group metal components supported on a refractory metal oxide support. (emphasis added)

9. As stated in the Final Office Action at pages 4-5, Shelef is applied to allegedly teach an automotive catalyst system comprising a substrate; a gamma-alumina washcoat support material; a substantially atomic layer of lanthana deposited on said alumina; a layer of oxygen storage material deposited on said lanthana coating; and at least a partial layer of catalytic material deposited on said oxygen storage material. (emphasis added)

10. Shelef does not teach or suggest a second washcoat layer deposited on a first washcoat layer, the second washcoat layer comprising an oxygen storage component and a binder therefor, and a third washcoat layer deposited on the second washcoat layer, the third washcoat layer comprising a platinum group metal component supported on a refractory oxide support. Instead, Shelef discloses the use of a gamma-alumina washcoat having an atomic layer of lanthana on the alumina (col. 2, lines 50-64). Thereafter, Shelef disposes an oxygen storage component by impregnation or incipient wetness over the lanthana atomic layer (col. 3, lines 24-29). Finally, a third layer precious metal is impregnated over the oxygen storage component layer (col. 3, lines 40-50).

11. Shelef fails to disclose or suggest disposing the oxygen storage component as a second washcoat layer over the first washcoat layer, and then disposing a third washcoat layer over the second washcoat layer. In the Final Office Action, it is stated that "Shelef clearly teaches the same number of catalyst layers containing the same metal components, which deposited on the same substrate material being required." (Final Office Action, page 6). This statement fails to give meaning to the phrase "washcoat layer" in the claims pending in the instant patent application.

12. Impregnation of a gamma-alumina support with lanthana, followed by impregnation with an oxygen storage component layer, followed by the impregnation of a precious metal layer, as described in Shelef, results in a different catalyst structure than claimed in the instant patent application. As described in the book, Catalytic Air Pollution Control, at pages 5-6 (attached as

Exhibit A), an impregnation processes results in the distribution of salt precursors into the pores of the alumina washcoat. This is shown in Figure 1.2 on page 6 of the book, in which Pt has been deposited into the pores of the alumina support particles. The Pt particles are represented as black dots. Importantly, the sentence bridging pages 5 and 6 of the book states:

“When the  $\text{Al}_2\text{O}_3$  is bonded to a monolithic honeycomb support, which will be described in Chapter 2, it is called a *washcoat*.” (emphasis in original).

13. The definition of a washcoat layer is also provided on pages 18-19 (attached as Exhibit B) of the book, which states with reference to Figure 2.2 on page 18 that, “The catalyzed coating is composed of a high-surface-carrier such as  $\text{Al}_2\text{O}_3$  impregnated with a catalytic components [sic]. This is referred to as the *catalyzed washcoat*.” (emphasis in original). Figure 2.2 shows a double-layered washcoat structure on a ceramic substrate, and it is clear from the optical micrographs that each washcoat layer comprises support particles. Thus, a washcoat layer is defined as a coating that is comprised of support particles. A catalyzed washcoat layer is a coating comprised of support particles impregnated with catalytic components.

14. The definition of a washcoat layer provided in the book is completely consistent with the meaning a person having ordinary skill in the art of catalyst manufacture would give to the phrase “washcoat layer” in the claims. For example, it is clear from the language of claim 1 that the first washcoat layer includes a refractory metal oxide and the third washcoat layer include a refractory metal oxide support. This definition of a washcoat layer is further supported in the specification at least at page 3, lines 24-31, which states that “washcoat compositions typically contain[ing] at least a refractory oxide support such as activated alumina.” Numerous other sections of the specification of the instant patent application support this definition of a washcoat layer, and include page 16, lines 1-19 and page 17, lines 22-24.

15. Claim 1 of the instant patent application is further distinguished over Shelef in that claim 1 requires the second washcoat layer to include a binder. It is noted that the second washcoat layer may comprise bulk particles of the oxygen storage component material, as explained at page 14, lines 15-29 and page 16, lines 1-11. The presence of a binder in the present application allows the oxygen storage component washcoat to bind to the underlying refractory metal oxide washcoat. Shelef does not disclose such a binder.

16. In summary, the Shelef reference cited in the Final Office Action does not teach or suggest all of the limitations of the claimed invention, namely an exhaust gas treatment catalyst comprising: (a) a carrier; (b) a first washcoat layer deposited on the carrier, said first washcoat layer comprising substantially only at least one refractory metal oxide; (c) a second washcoat layer deposited on the first washcoat layer, said second washcoat layer comprising substantially only at least one oxygen storage component and at least one binder therefor; and (d) a third washcoat layer deposited on the second washcoat layer, said third washcoat layer comprising at least one layer of one or more platinum group metal components supported on a refractory metal oxide support.

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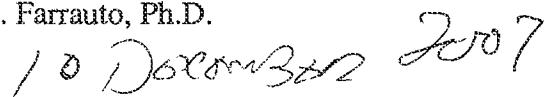
Page 4

17. I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment or both under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patents that may issue thereon.



Robert J. Farrauto, Ph.D.

Date:



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# **CATALYTIC AIR POLLUTION CONTROL**

## **Commercial Technology**

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**Second Edition**

**Ronald M. Heck and Robert J. Farrauto  
with Suresh T. Gulati**



**A JOHN WILEY & SONS, INC., PUBLICATION**

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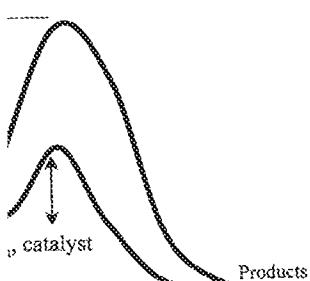
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ion coordinate  
reaction energy paths for reactants converted to  
reaction is lowest.

$\propto$  is proportional to the number of active  
e universal gas constant and the absolute

$$= k C_a^x C_b^y \quad (1.3)$$

$$\exp\left(-\frac{E}{RT}\right) \quad (1.4)$$

reaction represents the slowest of all steps  
products. The overall rate can never be  
difference between the energy states of the  
mic heat of reaction.

catalyst functions to decrease the activa-  
rtant environmental application of the ox-  
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in the absence of a catalyst, because the  
ciation of  $O_2$  into  $O$  atoms. The activation  
nently to be about 40 kcal/mol. In the  
on of  $O_2$  occurs catalytically on the metal  
ecomes the reaction of adsorbed  $CO$  with  
energy is reduced to less than 20 mol/mol  
hus, the catalyst changed the rate-limiting  
ath for the product to be formed. The cat-  
ind lowers the energy necessary for the re-

action. This is a key reason why  $CO$  can be abated from vehicles and power  
plants at modest temperatures.

It is of great importance to recognize that neither the net enthalpy nor the  
net free energy is affected by the presence of the catalyst. A catalyst changes  
neither the energetics of the initial and final states nor the equilibrium, but af-  
fects only the rate of approach to the final product state. The catalyst enhances  
the kinetics of reaching equilibrium. Thus, the reaction enthalpy,  $\Delta H$ , and re-  
action free energy,  $\Delta G$  (and consequently the equilibrium constant,  $K_e$ ) are not  
altered by the presence of a catalyst.

The catalyst influences selectivity by preferentially lowering the activation  
energy for a particular step in the reaction sequence and increases the rate at  
which this step proceeds. Selectivity is an issue for many reactions in which  
multiple products can occur in parallel. For the example with the  $V_2O_5$  cata-  
lyst, the reaction path leading to the formation of the aldehyde product is fa-  
vored because it has a lower activation energy than the complete combustion to  
 $CO_2$  and  $H_2O$ . For the reaction using Pt the opposite is true. It is the job of the  
catalyst to reduce the activation energy of the reaction that will yield the desir-  
able product.

In catalytic air pollution control, all the processes utilize solid heterogeneous  
catalysts through which gaseous reactants pass. This is distinguished from a  
homogeneous liquid-phase catalyst, which is soluble in the reaction medium.

## 1.2 DISPERSED CATALYST MODEL

In many industrial reactions, the number of reactant molecules converted to  
products in a given time is directly related to the number of catalytic sites  
available to the reactants. It is, therefore, common practice to maximize the  
number of active sites by dispersing the catalytic components onto a surface.  
Maximizing the surface area of the catalytic components, such as Pt, Fe, Ni,  
Rh, Pd,  $CuO$ ,  $PdO$ , and  $CoO$ , increases the number of sites on which chem-  
isorption and catalytic reaction can occur. It is common practice to disperse the  
catalytic components on a high-surface-area carrier, such as  $Al_2O_3$ ,  $SiO_2$ ,  $TiO_2$ ,  
and  $SiO_2-Al_2O_3$ . In some cases, but not for environmental applications, non-  
oxides such as high surface area carbons are also used as carriers. The carriers  
themselves seldom are catalytically active, but do play a major role in main-  
taining the overall stability and durability of the finished catalyst.

The preparation and properties of these materials and their influence on  
catalytic reactions will be discussed in Chapter 2, but, for now,  $Al_2O_3$  (the most  
commonly used carrier in catalysis, especially for environmental applications)  
will be used to develop a model of a heterogeneous catalyst. Figure 1.2 illus-  
trates a few select pores of a high-surface-area  $Al_2O_3$ .

Figure 1.2 shows 20- and 100- $\text{\AA}$  pores into which Pt has been deposited by  
solution impregnation. The Pt particles or crystallites are represented as dots.  
When the  $Al_2O_3$  is bonded to a monolithic honeycomb support, which will be

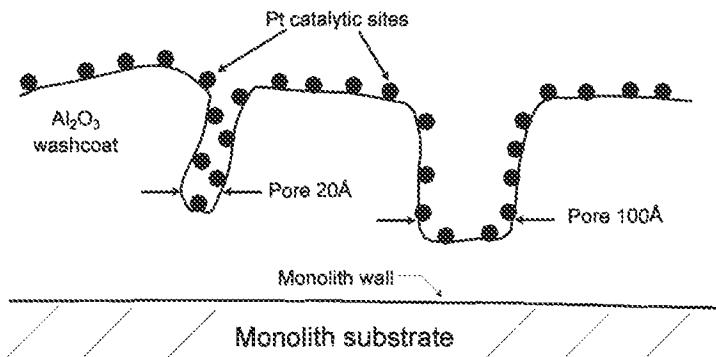


Figure 1.2 Conceptual model for catalytic sites dispersed on a high-surface-area  $\text{Al}_2\text{O}_3$  carrier bonded to a monolith.

described in Chapter 2, it is called a *washcoat*. The internal surface of the  $\text{Al}_2\text{O}_3$  is rich in surface  $\text{OH}^-$  (hydroxyl) groups (not shown), depending on the type of  $\text{Al}_2\text{O}_3$  and its thermal history. These  $\text{OH}^-$  species, which cover the entire surface and are part of the walls of each pore, represent sites on which one can chemically or physically bond a catalytic substance. The physical surface area of the  $\text{Al}_2\text{O}_3$  is the sum of all internal areas of the oxide from all the walls of each and every pore. It is on these internal walls and at the  $\text{OH}^-$  sites that the catalytic components are bound. The catalytic surface area is the sum of all the areas of the active catalytic components in this example, Pt. The smaller the individual size of the crystallites of the active catalytic material (higher catalytic surface area), the more sites are available for the reactants to interact. As a rough approximation, one assumes that the higher the catalytic surface area, the higher the rate of reaction for a process controlled by kinetics rather than mass transfer.

The tiny Pt-containing particles shown in Figure 1.2 are dispersed throughout the porous  $\text{Al}_2\text{O}_3$  carrier network and generate a high-Pt surface area. This procedure maximizes the catalytic area but also introduces other possible rate controlling physical processes such as mass transfer of the reactants to the catalytic sites. Each of these processes has a rate influenced by the hydrodynamics of the fluid flow, the pore size and structure of the carrier, and the molecular dimensions of the diffusing molecule (Farrauto and Bartholomew 1997; Morbidelli et al. 2001). These are discussed below.

### 1.3 THE STEPS IN HETEROGENEOUS CATALYSIS

To maximize reaction rates, it is essential to ensure accessibility of all reactants to the active catalytic sites dispersed within the internal pore network of the

This method is particularly effective for the precious metals because they are easily reduced to their metallic states. The advantage of the reducing agents mentioned above is that, on subsequent heat treatment, they leave no residue.

### 2.3.3 Drying

Excess water and other volatile species are removed during forced air drying at about 110°C.

### 2.3.4 Calcination

It is most common to calcine the catalyst in forced air to about 400–500°C to remove all traces of decomposable salts used to prepare the catalyst.

## 2.4 NOMENCLATURE FOR DISPERSED CATALYSTS

The combination of the catalytic species supported on a carrier is presented by stating the amount and specific catalytic material, followed by the chemical formula of the carrier separated by a slash, such as 0.5% Pt/SiO<sub>2</sub>, 1% Pd/Al<sub>2</sub>O<sub>3</sub>, and 3% V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub>. It must be clearly understood that this describes only the general composition of the catalyst and not the nature or chemistry of the active sites responsible for the particular catalytic reaction. These are seldom known in real processes.

## 2.5 MONOLITHIC MATERIALS AS CATALYST SUBSTRATES

Monolithic or honeycomb materials offer a number of advantages over more traditional pellet-shaped catalysts and, thus, are now widely used as supports in environmental applications. It is a unitary structure composed of inorganic oxides or metals in the structure of a honeycomb with uniform-sized and parallel channels that may be square, sinusoidal, triangular, hexagonal, round, and so on. Various monolith properties in Chapters 3, 7, and 9, will be discussed, but for now it suffices to say monolithic structures are available as ceramic and metal with different channel dimensions and shapes.

Commercial ceramic monoliths have large pores and low surface areas (e.g., 0.3 m<sup>2</sup>/g), so it is necessary to deposit a high-surface-area carrier, which is subsequently catalyzed, onto the channel walls. The catalyzed coating is composed of a high-surface-carrier such as Al<sub>2</sub>O<sub>3</sub> impregnated with a catalytic components. This is referred to as the *catalyzed washcoat*. Figure 2.2 shows various magnifications of a 400 cells per square inch (cpsi) ceramic monolith with a double washcoat commonly used in automotive applications.

The washcoat can be seen deposited over the entire wall, but it is con-

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talyst in forced air to about 400–500°C to alts used to prepare the catalyst.

### SPERSED CATALYSTS

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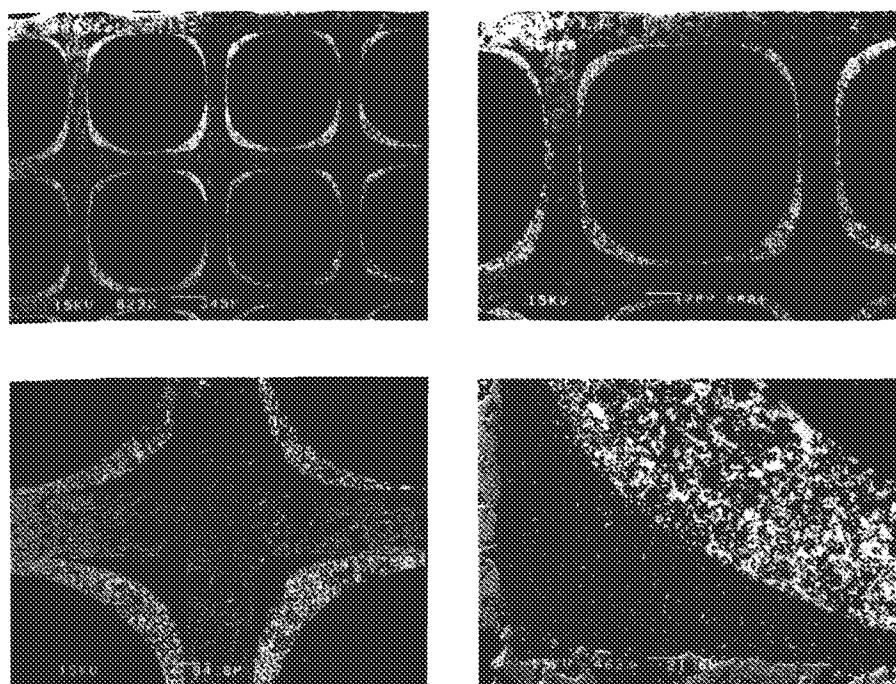


Figure 2.2 Optical micrographs of double-layered washcoated ceramic monoliths.

centrated at the corners of the square channel ceramic monolith. The thickness of the “fillet” depends primarily on the geometry of the channel and the coating method. The pollutant-containing gases enter the channels uniformly and diffuse through the washcoat pore structure to the catalytic sites where they are converted catalytically. The amount of geometric surface area, on which the washcoat is deposited, is determined by the number and diameter of the channels. There is a limit as to how much washcoat can be deposited, since an excessive amount results in a decrease of the effective channel diameter, thereby increasing the pressure drop to an unacceptable level.

Monoliths offer a number of engineering design advantages that have led to their widespread use in environmental applications. However, one of the most important is low-pressure drop associated with high flow rates. The monolith has a large open frontal area and with straight parallel channels offers less resistance to flow than does a pellet-type catalyst. Low-pressure drop translates to lower compressor costs for stationary applications and greater power saving for mobile sources. Other advantages include excellent attrition resistance, good mechanical properties, compact, and freedom in reactor orientation.

A more detailed description of monoliths will be presented in Chapters 7 and 9.

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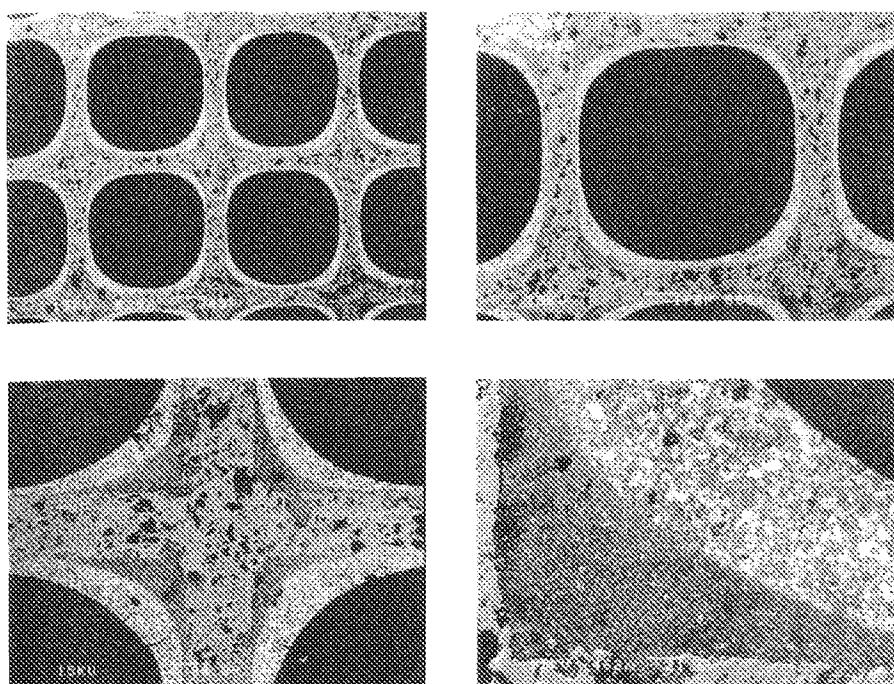


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